NOLTR 67-66

THE CHEMISTRY OF DETONATIONS. I.

A SIMPLE METHOD FOR CALCULATING DETONATION PROPERTIES OF C-H-N-O EXPLOSIVES

AUGUST 1967

NOL

UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

NOLTR 67-66

NOLTR 67-66

The Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of C-H-N-O Explosives

Mortimer J. Kamlet and S. J. Jacobs

U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland

ABSTRACT.- Detonation pressures of C-H-N-O explosives at initial densities above 1.0 g/cc may be calculated by means of the simple empirical equation, $P = K\rho_o^2\varphi$, $K = 15.58$, $\varphi = NM^{\frac{1}{2}}Q^{\frac{1}{2}}$; detonation velocities by the equation, $D = A\varphi^{\frac{1}{2}}(1 + B\rho_o)$, $A = 1.01$, $B = 1.30$. N is the number of moles of gaseous detonation products per gram of explosive; M is the average molecular weight of these gases; Q is the chemical energy of the detonation reaction (ΔH_o per gram); and ρ_o is the initial density. Values of N, M and Q may be estimated from the $[H_2O\text{-}CO_2]$ arbitrary decomposition assumption, so that the calculations require no other input information than the explosive's elemental composition, heat of formation and loading density. Detonation pressures derived in this manner correspond quite closely to values predicted by a computer code known as RUBY, which employs the most recent parameters and covolume factors with the Kistiakowsky-Wilson equation of state.

APPROVED BY: J. E. ABLARD
CHEMISTRY AND EXPLOSIVES
RESEARCH AREA
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

NOLTR 67-66

THE CHEMISTRY OF DETONATIONS. I. A SIMPLE METHOD FOR CALCULATING DETONATION PROPERTIES OF C-H-N-O EXPLOSIVES.

This report is the first of a series which describes simplified methods of predicting detonation parameters and, eventually, certain types of damage effects of C-H-N-O high explosives using as a priori information only a knowledge of their chemical structure. It is hoped that the relationships described herein will be useful to the synthesis chemist in designing new more-efficient explosives. The work was carried out under the Foundational Research Program of this Laboratory.

E. F. SCHREITER
Captain, USN
Commander

J. E. Ablard

J. E. ABLARD
By direction

CONTENTS

ILLUSTRATIONS

TABLES

I. INTRODUCTION

To a chemist concerned with the synthesis of new high explosive compounds the ability to compute detonation properties (detonation pressure, energy, and velocity as well as product composition) from a given molecular structure and the known or estimated crystal density is a problem of the utmost importance. The calculated properties could be meaningful in the decision as to whether it is worth the effort to attempt a new and complex synthesis. One reason behind the recent development of detonation properties programs for use on high speed computers has been to supply this desired information. One such program, the RUBY code[1], has recently been made available to a number of laboratories, the authors' included.

In an effort to understand the formidable appearing output of many computations for a wide variety of C-H-N-O explosives at various initial loading densities, we have investigated interrelationships between such properties as pressure, velocity, density, heat of reaction, etc. These studies have led to a number of interesting observations, important among which were the "facts" that much simpler semi-empirical formulas could be written for desk calculation of detonation velocities and detonation pressures, with about the same reliance on their answers as one could attach to the more complex computer output. These equations require as input information only the explosive's composition and loading density and an estimate of its heat of formation and, in their comparative simplicity, seem to throw light on the relative importance of the quantities which determine the detonation pressure in particular, and other properties as well.

It is hoped that the present findings may give those untrained in the details of the thermodynamic-hydrodynamic calculations a better "feel" for the

results of the computor output. A further hope is that these papers will also serve as a reminder to users of "black box" computation schemes to the effect that "the output is no better than the input and the responsibility for the input still rests largely with the user, not the box maker".

II. DETONATION CALCULATION

In the last 25 years, calculations of the detonation properties of condensed explosives from their chemical compositions and densities have been approached in various ways.[3] All have used the necessary conservation conditions for steady flow with the detonation discontinuity satisfying the Chapman-Jouguet hypothesis (minimum detonation velocity compatible with the conservation conditions or sonic flow behind the discontinuity in a reference frame where the discontinuity is at rest). In order to describe the product state and the thermodynamic variables which fix its composition, an equation of state applicable to a very dense state is required. To apply this equation to a mixture of gaseous and solid products, a mixing rule is also needed and the temperature must be explicitly defined. Consequently, the choice of equation of state to be used for the "gaseous" products must be somewhat more general than the equations used to describe properties on an isentrope from the detonation state. Of the several equation of state approaches used, only three will be mentioned here.

First, we consider the virial expansion in density originally due to Boltzmann[2,3] derived from the kinetic theory of gases for hard sphere molecules. This equation was modified by Hirschfelder and Roseveare[3] and covolume terms for product species were adjusted to high temperature[4,5] by setting them equal to the high temperature second virial coefficients. The equation is:

$$PV_g/RT = 1 + x + .625\,x^2 + .2869\,x^3 + .1928\,x^4 \qquad (1a)$$

with

$$x = b/V \quad ; \qquad b = \Sigma x_i b_i \tag{1b}$$

b_i is the molar covolume of the ith specie,

x_i is the mole fraction of the ith specie,

V_g is the molar volume of the gas mixture, and

P, T and R are the pressure, temperature, and gas constant.

The b_i are derived from the collision radii of the molecular species at high temperature and, as in the kinetic theory of gases at moderate pressure, are equal to four times the molecular volume multiplied by Avogadro's number. Despite the use of diminished covolumes in the equation and despite the apparent theoretical basis of the model, the equation is oversimplified and the results on detonation calculations quite clearly show it to be inaccurate.

The virial expansion in the pressure was used by Jones and Miller[6]. Their equation is:

$$PV_g = RT + bP + cP^2 + dP^3 . \tag{2}$$

The constants b, c, and d for this equation were fitted by the authors to give the correct detonation velocity (D) vs initial density (ρ_o) behavior for the explosive described (TNT). Although this relationship is empirical and the constants are fixed by detonation data, the equation exhibits solid-like properties, e. g., an internal energy term due to molecular repulsion at high pressure, and to this extent appears to describe the state of a high density gas better than Equation (1). That this equation has not been widely used by others may have as its reason that the constants may not be generally applicable to all compositions. If the constants require known detonation velocity data for their determination, the equation would not be suitable for a priori calculations from composition and density.

A third approach, instigated by Kistiakowsky, Wilson and Halverson[7], may

be said to have its roots in Eq. (1). These authors modified an equation due to Becker,

$$P = RT(1 + Xe^{X})/V + f(V); \quad X = b/V, \tag{3}$$

by dropping the f(V) dependence, adding an adjustable constant, β, and making b a function of temperature. This "variable covolume" equation, as further modified by Fickett and Cowan[8], became:

$$PV_g/RT = 1 + Xe^{\beta X}, \tag{4a}$$

$$X = \kappa \Sigma x_i k_i / V_g (T + \theta)^{\alpha}. \tag{4b}$$

Eq. (4) is a variable covolume departure from the hard-sphere-molecule Eq. (1), for if $\beta = 0.625$, $\kappa = 1$ and $\alpha = 0$ the K-W equation would be identical with the Boltzmann equation to the third virial term and the k_i's would be just the b_i's of the hard-sphere-molecule model. If β were 0.625, with α about 0.25 to 0.5, one might consider the K-W equation to be a "soft-sphere" equation of state. In applying Eq. (4) to calculation of detonation velocities it was quickly found, however, that β could not be as large as 0.625 and, in the earlier papers on this problem[7,9,10], the values adopted were $\kappa = 1.0$, $\beta = 0.3$, $\alpha = 0.25$ and $\theta = 0$.

With these parameters and the D-ρ_o data for a number of explosives, k_i's were determined for the principal molecular species expected as detonation products from C-H-N-O explosives. The values obtained came fairly close to agreeing with the b_i's of Eq. (1) if one defined b_i as,

$$b_i = \kappa k_i / (T + \theta)^{\alpha}, \tag{5}$$

and assumed $T = 4000^{\circ}$ as typical of detonation temperatures found. Computations were made by estimating fixed detonation product compositions as well as on the basis of equilibrium calculations. The equilibrium calculations of Brinkley and

Wilson[9] tended, at that time, to favor an [H_2O–CO–CO_2] "arbitrary" method of estimating detonation product compositions. Consequently, Snay and Christian[10] tried both [H_2O–CO–CO_2] and [CO–H_2O–CO_2] arbitrary decomposition schemes to test the effects of changing composition on predicted detonation properties and covolume factors. By least squares they determined a best set of covolume factors for the above parameters. The results were not very much influenced by the decomposition assumption, but computed detonation pressures were lower than values found experimentally.

The next step toward better fitting of the K-W equation to detonation data was made by Cowan and Fickett[8], who established a substantially different set of parameters and covolume factors. More recent adjustments by Mader[11] have led to the parameter sets used most frequently today in the RUBY code. Mader's parameters were designed to give the best match with five experimental measurements considered to be highly accurate: the detonation pressure of RDX at 1.8 g/cc, the detonation velocities of RDX at 1.0 and 1.8 g/cc, and the detonation velocities of TNT at 1.0 and 1.64 g/cc. Fundamental difficulties in finding a single set of parameters to accomodate these five measurements led Mader to suggest dual sets of β and κ: an "RDX parameter set" to be used with compounds producing lesser amounts of solid carbon in the detonation, a "TNT parameter set" with explosives producing greater amounts of solid carbon (Table I).

Table I. Parameters in Eq. (4)

Source	ref.	α	β	κ	θ
Kistiakowsky-Wilson Brinkley-Wilson Christian-Snay	7 9 10	0.25	0.3	1.0	0
Cowan-Fickett	8	0.5	0.09	11.85	400
Mader, RDX	11	0.5	0.16	10.91	400
Mader, TNT	11	0.5	0.096	12.69	400

It should be said that only since Cowan and Fickett's report has good experimental detonation pressure data been available for use in arriving at best-fit parameters. Also, the covolume factors (k_i) have been deliberately normalized but not set equal to molecular excluded volumes. In this normalization, rather cogent arguments were made for reducing the orientation effect of the polar molecules (H_2O and NH_3 in particular), and thereby increasing the magnitudes of the corresponding k_i's relative to those for non-polar molecules[12]. The result is an empirical equation which at this time is the best available for general detonation state calculations.

Three significant consequences in regard to detonation calculations on C-H-N-O compositions derive from the present K-W parameters and covolume factors: the predicted detonation temperature is quite low; the predominant carbon-oxygen product is CO_2 rather than CO over a wide range of compositions at the higher loading densities; the detonation pressure and velocity are reasonably close to experiment wher experimental data are available. Whether the result on CO_2 is correct or not, it has served as one point of departure for the discussion which follows.

III. THE COVOLUME FACTOR - MOLECULAR WEIGHT RELATIONSHIP

The covolume factors most recently used by Mader[11] for H_2O, CO_2 and N_2 (and thus, by inference, for isoelectronic CO) were further adjusted from Cowan and Fickett's values[8] so as best to reproduce experimental Hugoniots[13-15], i. e. H_2O, 360 → 250; CO_2, 670 → 600; N_2, 380 → 380; CO, 390 → 390. The k_i's for the "minor" detonation species, CH_4, H_2, NO and O_2, in current K-W detonation computations remain the "theoretical" values deriving from calculated molecular dimensions. In the light of this fact and because H_2O, CO_2, N_2 and CO are usually considered to comprise 96+% of the detonation gases from organic C-H-N-O explosives

it is noteworthy that Mader's k_i's for the "major" detonation species are closely proportional to their molecular weights (Table II).

Table II. The Covolume Factor-Molecular Weight Relationship for the Major Detonation Species

Specie	k_i	k_i / M_i
H_2O	250	13.89
N_2	380	13.57
CO	390	13.93
CO_2	600	13.64
	average	(13.76 ± 0.15)

This observation is of substantial interest in view of Christian and Snay's report[10] that empirical covolume factors for the total gas mixtures of twenty organic explosives, chosen to give best average agreement between calculated and measured detonation velocities, were also roughly proportional ($\pm$ ca 4%) to the average molecular weights of the assumed gaseous detonation products. Taken in combination, these findings have suggested that, for most organic C-H-N-O explosives, $\Sigma x_i k_i$ in the Kistiakowsky-Wilson equation may be replaced by the product H·M, where H is the constant, 13.76, and M is the average gas molecular weight. Since $(M/V_g) = \rho_g$, ρ_g being the density of the gaseous products in the detonation state, this allows transformation of Eq. (4) to:

$$P = (RT\rho_g/M)(1 + Xe^{\beta X}), \quad X = \varkappa H \rho_g / (T + \theta)^{\alpha} . \qquad (6)$$

We now introduce two terms which will become very important in subsequent discussions: N, the number of moles of gaseous detonation products per gram of explosive, and G, the weight fraction of explosive going over to gaseous products. From the definitions, N·M = G, so that after combining constants, $\varkappa H = A$ and $\beta\varkappa H = B$, the equation may now take the general form:

$$P = \frac{N R T \rho_g}{G}\left[1 + \frac{A \rho_g}{(T+\theta)^{\alpha}}\, e^{B\rho_g/(T+\theta)^{\alpha}}\right] \qquad (7)$$

The various factors influencing P in the K-W equation may be assessed more readily when it takes the form of Eq. (7) in which the k_i terms are eliminated than had been the case with Eq. (4). As an example, the dependence of P on T resulting from the use of Mader's "RDX parameters" is evaluated at various loading densities in Appendix I for a special case of Eq. (7).

IV. THE RUBY COMPUTER CODE

With the advent of the new high-speed digital computers, several more sophisticated methods of predicting detonation properties of high explosives from the Kistiakowsky-Wilson equation of state have achieved wide acceptance. Two related programs, the STRETCH BKW code for use on the IBM-7030 computer[11] and the RUBY code[1] for use on the IBM-7090 provide the comparison information against which predictions from the equations offered in the present paper will be judged. For the purposes of present discussions, RUBY results as determined at the Naval Ordnance Laboratory[16] and STRETCH BKW results differ only in minor regards[17]. Unless otherwise specified, therefore, the term RUBY shall hereafter encompass the results of both systems and RUBY computations shall be considered as based on Mader's most recent parameters and covolume factors in Eq. (4), with the heat of formation of solid carbon taken as zero.

The RUBY code finds "exact" equilibrium compositions of the detonation products by sophisticated multi-iterative processes involving minimization of the Gibbs free energy of the total system. Complex input equations, derived through the equation of state, relate free energies of formation of the potential detonation products to temperatures, pressures, covolumes and the compressibility of solid carbon. The current codes are equipped to consider as many as sixteen

gaseous products and two solid phases; improved codes are being designed to accomodate sixty gaseous species and five solid phases[16].

Several pages of print-out are associated with a single RUBY computation. Reported together with D, P, T and V_g at a given ρ_o (loading density) are the following quantities: ΔE_o, the chemical energy of the detonation reaction ($\approx Q$); $E_J - E_o$, the change in internal energy across the detonation front; ρ_J, the Chapman-Jouguet density; N, the total number of moles of gaseous detonation products per gram of explosive; N_i, the number of moles of the individual gas species; N_s, the number of gram-atoms of solid carbon or other solids; V_s, the solid volume per gram-atom carbon; and γ, the "gamma law" constant, $\gamma = (-\partial \ln P / \partial \ln V)_s$. Although only P, D and possibly T are subject to relatively unambiguous experimental verification at the current "state-of-the-art", RUBY's predictions of other of the above quantities provide a framework upon which much of the subsequent discussion is based.

V. SIMPLE EQUATIONS FOR ESTIMATING DETONATION PROPERTIES

We have found that estimates of detonation pressure and velocity, corresponding surprisingly closely to RUBY predictions, are possible for C-H-N-O explosives by means of relatively simple empirical equations. These equations imply that the "mechanical" properties of the detonation depend only on the number of moles of detonation gases per unit weight explosive, the average molecular weight of these gases, the chemical energy of the detonation reaction ($Q = \Delta H_o$), and the loading density, with the dependence in each case being relatively simple. The equations take the forms,

$$P = K\rho_o^2\varphi , \quad K = 15.58, \quad \varphi = NM^{\frac{1}{2}}Q^{\frac{1}{2}} , \tag{8}$$

and

$$D = A\varphi^{\frac{1}{2}}(1 + B\rho_o) , \quad A = 1.01, \quad B = 1.30 \tag{9}$$

where P is expressed in Kbar, D in mm/usec, N in moles gas/g explosive, M in g gas/mole gas, Q in cal/g and ρ_0 in g/cc.

As a first test of these equations, values of N, M and Q are taken from RUBY print-outs as reported by Hurwitz[16] to compare P_{calc} (Eq. 8) and D_{calc} (Eq. 9) with P_{RUBY} and D_{RUBY} for several representative explosives at typical loading densities. The results are given in Table III.

Table III near here.

It is seen that substituting N_{RUBY}, M_{RUBY} and Q_{RUBY} into Eqs. (8) and (9) leads to detonation pressures and velocities which differ only nominally from values predicted by the computer. The problem of a suitable method for simple hand-calculation of these detonation properties resolves itself to finding a reasonable scheme for estimating N, M and Q without the assistance of the computer

VI. ESTIMATION OF N, M AND Q; THE [H_2O-CO_2] ARBITRARY

Product compositions at the Chapman-Jouguet state and in the subsequent expansion of the detonation gases depend most strongly on the two important equilibria,

$$2\ CO \rightleftharpoons CO_2 + C\ , \quad \Delta H_0 = -41.2\ \text{Kcal}, \tag{10}$$

$$H_2 + CO \rightleftharpoons H_2O + C\ , \quad \Delta H_0 = -31.4\ \text{Kcal}. \tag{11}$$

From Le Chatelier's principle, higher pressures (higher densities) should shift these equilibria to the right, higher temperatures to the left. Since RUBY treats carbon as a condensed phase (and thus of unit activity), its amount does not materially affect the equilibria and, so long as at least some solid carbon appears, the ratios (CO_2/CO) and (H_2O/H_2) are rough measures of the equilibrium positions. RUBY's predictions of these ratios for some typical explosives are given in Table IV.

Table III. Comparison of Eqs. (8) and (9) with RUBY Results; N, M and Q Taken from RUBY Print-Outs[a].

Explosive[b]	ρ_o	N_{RUBY}	M_{RUBY}[c]	Q_{RUBY}	P_{calc} Eq. (8)	P_{RUBY}	% diff	D_{calc} Eq. (9)	D_{RUBY}	% diff
HMX[d]	1.903	0.0338	27.20	1496	384.7	391.3	-1.7	9.157	9.238	-0.9
RDX[d]	1.712	0.0339	27.15	1496	311.9	306.0	+1.9	8.512	8.437	+0.9
TNT[e]	1.468	0.0263	27.94	1258	165.5	161.2	+2.7	6.512	6.446	+1.2
Tetryl[d]	1.643	0.0276	30.06	1411	239.1	235.9	+1.4	7.548	7.508	+0.5
Explosive D[e]	1.720	0.0285	28.27	1098	231.4	227.3	+1.8	7.312	7.250	+0.8
Picramide[e]	1.770	0.0265	29.89	1250	250.0	245.6	+1.8	7.541	7.392	+2.0
R-Salt[e]	1.520	0.0345	23.08	1397	223.0	221.2	+0.8	7.478	7.444	+0.5
DINA[d]	1.660	0.0335	26.93	1450	284.2	276.9	+2.6	8.203	8.143	+0.7

Footnotes to Table III:

a) Hurwitz, Ref. 16.
b) See Appendix II for glossary of compound names and molecular formulas.
c) M_{RUBY} is calculated from the relationship, $M = (1 - 12 N_s)/N_{RUBY}$.
d) Computor results based on RDX parameters.
e) Computor results based on TNT parameters.

Table IV. Detonation Product Ratios as Predicted by RUBY

Explosive	Product Ratio	Loading Density, g/cc 1.0	1.2	1.4	1.6	ρ_x
TNT, $\rho_x = 1.64$	CO_2/CO	0.56	1.00	2.74	7.13	8.83
	H_2O/H_2	27.8	93.9	373	1981	2497
HMX, $\rho_x = 1.9$	CO_2/CO	0.37	0.94	2.73	10.52	254
	H_2O/H_2	26.0	118.4	754	8894	10^6
Tetryl $\rho_x = 1.7$	CO_2/CO	0.47	1.05	2.57	7.76	15.41
	H_2O/H_2	24.8	91.2	412	2876	10^4
DATB $\rho_x = 1.788$	CO_2/CO	0.60	1.35	3.30	9.38	31.26
	H_2O/H_2	32.0	119.1	529	3298	10^4

As is shown, the computer predicts high (H_2O/H_2) ratios for C-H-N-O explosives at $\rho_0 > 1.0$ g/cc so that, for practical calculational purposes, equilibrium (11) may be considered as invariently to the right at all loading densities under consideration[19]. The [2 CO $\rightleftarrows$ CO_2 + C] reaction, on the other hand, is in a region of shifting equilibrium and may be considered as predominantly to the right only at the higher loading densities (i. e., greater than 1.6 or 1.7 g/cc.).

This study had as its original purpose to develop a simple method of intercomparing detonation properties of experimental C-H-N-O high explosives. Such materials generally have crystal densities of 1.7 - 1.9 g/cc, and are most often used at high proportions of theoretical maximum density. For these explosives it was therefore considered a reasonable first approximation to assume that equilibrium (10) was also to the right in the detonation state.

Provided that no other species than N_2, H_2O, CO_2, CO and H_2 are present in appreciable amounts in the detonation gases (and RUBY predicts less than 2 mole % extraneous species at 1.0 g/cc, lesser amounts at higher loading

densities), situations where equilibria (10) and (11) are each predominantly to one extreme or the other are described concisely by the various arbitrary assumptions of detonation product compositions. Thus the [H_2O–CO–CO_2] arbitrary, already mentioned, represents equilibrium (10) as being predominantly to the left and equilibrium (11) predominantly to the right; the [CO–H_2O–CO_2] arbitrary represents both equilibria as being predominantly to the left. In a like manner, the condition in Table IV at the higher densities, where equilibria (10) and (11) are both predominantly to the right, may be represented by an [H_2O–CO_2] arbitrary. The latter arbitrary, which will provide the basis for our estimating N, M and Q in the present calculations, predicts N_2, H_2O and CO_2, but not CO, as the important detonation products, with H_2O having priority in formation over CO_2.

Given an explosive compound or composition, $C_aH_bN_cO_d$, in which there is at least enough oxygen to convert hydrogen to H_2O but no more than is also required to convert carbon to CO_2, the [H_2O–CO_2] arbitrary calls for the formation of detonation products according to the following decomposition equation:

$$C_aH_bN_cO_d \longrightarrow \frac{c}{2} N_2 + \frac{b}{2} H_2O + \left(\frac{d}{2} - \frac{b}{4}\right) CO_2 + \left(a - \frac{d}{2} + \frac{b}{4}\right) C \ . \quad (12)$$

It follows then that,

$$N_{arb} = \frac{2c + 2d + b}{48a + 4b + 56c + 64d} \ , \quad (13)$$

$$M_{arb} = \frac{56c + 88d - 8b}{2c + 2d + b} \quad (14)$$

and since,

$$Q = -\Delta H_0 = \frac{-[\Delta H_f \text{ (detonation products)} - \Delta H_f \text{ (explosive)}]}{\text{formula weight}} \ , \quad (15a)$$

taking standard heats of formation for water (g), nitrogen and carbon dioxide and assuming the ΔH_f of solid carbon to be nil leads to,

$$Q_{arb} = \frac{28.9\,b + 47.0\,(d - b/2) + \Delta H_f\ (\text{explosive})}{12a + b + 14c + 16d} \,. \qquad (15b)$$

RUBY takes the NRT term into account in its detonation energy computations; for purposes of convenience, we ignore it in the arbitrary calculations. Thus, RUBY's Q represents ΔE_o; Q_{arb} represents ΔH_o. The difference amounts to 10-15 cal/g or about 1% of Q for a typical explosive.

Values of N_{arb} as calculated from Eq. (13) are compared in Table V with the corresponding RUBY predictions for a variety of explosives at loading densities from 1.0 to 1.9 g/cc.

Table V. Comparison of N_{arb} with N_{RUBY}

Explosive	ρ_o (ref.)	N_{arb}	N_{RUBY}	% diff
HMX	1.903 (16)	.0338	.0338	0.0
	1.808 (16)		.0338	0.0
	1.600 (11)		.0341	-0.9
	1.400 (11)		.0348	-2.9
	1.200 (11)		.0362	-6.6
	1.000 (11)		.0381	-11.3
PETN	1.780 (16)	.0316	.0318	-0.6
	1.600 (11)		.0320	-1.3
	1.400 (11)		.0333	-5.4
	1.200 (11)		.0348[a]	-9.2
Tetryl	1.730 (16)	.0270	.0273	-1.1
	1.642 (16)		.0276	-2.2
	1.400 (11)		.0285	-5.5
	1.200 (11)		.0301	-10.3
	1.000 (11)		.0322	-16.1
TNT	1.651 (16)	.0253	.0257	-1.6
	1.600 (11)		.0258	-2.0
	1.400 (11)		.0265	-4.8
	1.200 (11)		.0277	-8.7
	1.000 (11)		.0293	-13.7
DATB	1.780 (11)	.0278	.0279	-0.4
	1.600 (11)		.0281	-1.1
	1.400 (11)		.0287	-3.1
	1.200 (11)		.0298	-6.7
	1.000 (11)		.0313	-11.2

Footnote to Table V:
a) Solid carbon no longer appears; N_{RUBY} is about the same at lower densities.

The tabulated data, which represent a fair sampling of RUBY print-out results, confirm that N_{arb} corresponds closely to N_{RUBY} for C-H-N-O explosives at higher loading densities, and differs increasingly from N_{RUBY} as the densities decrease and equilibrium (10) shifts to the left. From these and additional data, average differences between N_{arb} and N_{RUBY} are: -0.3% at loading densities above 1.75 g/cc; -1.5% at 1.60 to 1.75 g/cc; -3.8% at 1.40 g/cc; -7.4% at 1.20 g/cc; and -11.9% at 1.00 g/cc. Differences between M_{arb} and M_{RUBY} and between Q_{arb} and Q_{RUBY} are correspondingly small at the higher densities and become correspondingly greater as the densities decrease.

Because it was considered that the intrinsic inexactness of the computer's input information led to uncertainties of at least $\pm 5\%$ in RUBY's predictions of P, we originally felt that differences of about the same magnitude between arbitrary N, M and Q and RUBY's values could be tolerated in the present study. For this reason the analyses of Tables IV and V led us to set $\rho_o = 1.4$ g/cc as a tentative lower limit of applicability of the present calculational method. The results below show this restriction to be unnecessary.

VII. RESULTS

Eqs. (8) and (13-15) provide the basis for a simple method of estimating detonation pressures, which requires as input information only the elemental composition, loading density, and an estimate of the heat of formation of the explosive. With the aid of a desk calculator, a typical calculation requires less than ten minutes. For comparison, two to four minutes of machine time are required for a routine RUBY computation on the IBM-7090 and a skilled operator requires an additional ten to fifteen minutes to prepare the input data and punch the cards.

Detonation pressures estimated by the simpler method are compared in Table VI with the corresponding RUBY values for twenty eight materials. Since we are

at this point concerned only with reproducing RUBY results, it is unimportant to the present discussion whether input heats of formation in the RUBY computations are accurate; although the ΔH_f for picric acid in ref. 11 has a misplaced decimal point, we have used the same incorrect value to estimate our Q_{arb}. Table VI also contains several other instances where differing estimates of ΔH_f in refs. 11 and 16 have led to our using two values of Q_{arb} for the same compound.

All available computer results for C-H-N-O explosives based on Mader's parameters and covolumes are included. In a number of cases two sets of RUBY results are listed: those based on the RDX parameters and those obtained using the TNT parameter set (Table I). Compounds in Table VI show Q_{arb} ranging from 525 to 1728 cal/g, M_{arb} ranging from 23.00 to 36.00 g/mole, N_{arb} ranging from 0.0238 to 0.0367 moles gas/g explosive and G_{arb} ranging from 0.722 to 1.000 g gas/g explosive, and are listed in order of decreasing G_{arb}. For reasons which will become obvious from inspection of the Table and from subsequent discussions, the Table includes results at loading densities down to 1.00 g/cc.

Table VI near here.

The hand-calculated detonation pressures in Table VI show good agreement with the RUBY values. Taking all "uncorrected" results, i. e., comparing the hand-calculated pressures with RUBY predictions based on both parameter sets, but excluding the values in parentheses for Compounds 1-6, differences between P_{calc} (Eq. 8) and P_{RUBY} average $\pm 2.89\%$ for the 127 data sets (28 explosives). Although this average difference falls well within RUBY's uncertainty limits, the Table includes 22 data sets wherein P_{calc} differs from P_{RUBY} by more than 5% and six data sets wherein the difference is greater than 10%. Since differences of comparable magnitudes may also be observed in Table VI between P_{RUBY} (RDX

Table VI. Comparison of P_{calc} (Eq. 8) with P_{RUBY} for C-H-N-O Explosives. Values of N, M and Q Estimated from the [H_2O-CO_2] Arbitrary.

Explosive[a] ρ_o (ref.)	φ_{arb}	P_{calc} (Eq. 8)[b]	RDX Parameters P_{RUBY}	% diff[b]	TNT Parameters P_{RUBY}	% diff
1. TNM, N = .0306, M = 32.67, Q = 525, G = 1.000						
1.640 (11)	4.007	167.8 (157.7)	162.5	+3.3 (-3.0)		
2. BTNEN, N = .0309, M =32.35, Q = 1298, G = 1.000						
1.862 (16)	6.332	342.1 (321.6)	319.0	+7.2 (+0.8)		
1.960 (16)		379.0 (356.3)	359.8	+5.3 (-1.0)		
3. NG, N = .0319, M = 31.32, Q = 1478, G = 1.000						
1.590 (11)	6.840	270.2 (254.0)	246.5	+9.6 (+3.0)		
4. BTNEU, N = .0311, M = 32.18, Q = 1481, G = 1.000						
1.767 (16)	6.789	330.4 (310.6)	308.1	+7.2 (+0.8)		
1.860 (16)		365.9 (343.9	346.8	+5.5 (-0.9)		
5. TNETB, N = .0298, M = 33.04, Q = 1479, G = 0.985						
1.000 (16)	6.587	102.6 (96.4)	93.3	+10.0 (+3.3)		
1.200 (16)		147.8 (138.9)	133.5	+10.7 (+4.0)		
1.400 (16)		201.2 (189.1)	183.2	+9.9 (+3.2)		
1.600 (16)		262.7 (246.9)	245.5	+7.0 (+0.6)		
1.691 (16)		293.5 (275.9)	274.6	+6.9 (+0.5)		
1.780 (16)		325.2 (305.7)	306.2	+6.2 (-0.2)		
6. PETN, N = .0316, M = 30.41, Q = 1525, G = 0.961						
1.000 (11)	6.805	105.9 (99.5)	101.6	+4.2 (-2.1)		
1.200 (11)		152.6 (143.4)	144.2	+5.8 (-0.6)		
1.400 (11)		207.8 (195.3)	196.4	+5.8 (-0.6)		
1.670 (11)		295.7 (278.0)	280.3	+5.5 (-0.8)	267.0	+10.7
1.770 (11)		332.1 (312.2)	318.8	+4.2 (-2.1)		
1.691 (16)		303.1 (284.9)	286.4	+5.8 (-0.6)		
1.780 (16)		334.3 (314.2)	321.0	+4.1 (-2.1)		
7. RDX, N = .0338, M = 27.20, Q = 1481, G = 0.919						
1.000 (11)	6.784	105.7	107.8	-1.9		
1.200 (11)		152.2	148.7	+2.4		
1.400 (11)		207.2	200.5	+3.3		
1.600 (11)		270.6	264.6	+2.3		
1.800 (11)		342.3	346.6	-1.2	324.0	+5.6
1.712 (16)		309.9	306.0	+1.3		
1.802 (16)		343.2	344.2	-0.3		
8. HMX, N = .0338, M = 27.20, Q = 1475, G = 0.919						
1.000 (11)	6.772	105.5	107.5	-1.8		
1.200 (11)		151.9	148.3	+2.4		
1.400 (11)		206.7	199.6	+3.6		
1.600 (11)		270.2	263.4	+2.5		
1.900 (11)		380.9	395.3	-3.6		
1.807 (16)		344.5	346.3	-0.5		
1.903 (16)		382.0	391.3	-2.4		

Table VI (continued)

9. DINA, N = .0333, M = 27.00, Q = 1438, G = 0.900							
	1.577 (16)	6.561	254.3	247.0	+2.9		
	1.600 (16)		261.7	255.1	+2.6		
	1.660 (16)		281.7	276.9	+1.7		
10. TNTAzB, N = .0268, M = 33.33, Q = 1643[c], G = 0.893							
	1.740 (11)	6.271	295.8	300.2	-1.5		
11. NQ, N = .0384, M = 23.00, Q = 901, G = 0.883							
	1.691 (16)	5.528	246.3			248.5	-0.9
	1.780 (16)		272.9			277.9	-1.8
12. EDNA, N = .0367, M = 24.00, Q = 1297, G = 0.880							
	1.663 (16)	6.473	278.7	285.8	-2.5	269.4	+3.5
	1.750 (16)		308.9	323.0	-4.4	300.8	+2.7
13. RDX/TNT, 77/23, N = .0318, M = 27.50, Q = 1436, G = 0.875							
	1.000 (11)	6.319	98.5	100.2	-1.7		
	1.200 (11)		141.8	139.0	+2.0		
	1.400 (11)		193.0	188.1	+2.5		
	1.600 (11)		252.0	250.2	+0.7		
	1.743 (11)		299.1	304.7	-1.9	288.0	+3.7
14. HMX/TNT, 76/24, N = .0318, M = 27.51, Q = 1429, G = 0.875							
	1.000 (11)	6.305	98.2	99.7	-1.5		
	1.200 (11)		141.5	138.4	+2.2		
	1.400 (11)		192.5	187.4	+2.6		
	1.600 (11)		251.5	249.8	+0.7		
	1.809 (11)		321.5	333.0	-3.5		
15. DNPN, N = .0322, M = 27.04, Q = 1407, G = 0.871							
	1.644 (16)	6.281	264.5	262.3	+0.8		
	1.730 (16)		292.9	295.1	-0.7		
16. HNsB, N = .0238, M = 36.00, Q = 1728[d], G = 0.857							
	1.700 (11)	5.936	267.2	272.3	-1.9		
17. NM, N = .0319, M = 31.32, Q = 1456, G = 0.853							
	1.128 (11)	6.769	134.1	130.3	+2.9		
18. HMX/TNT, 64/36, N = .0307, M = 27.68, Q = 1409, G = 0.850							
	1.000 (11)	6.063	94.5	95.8	-1.5		
	1.200 (11)		136.1	133.6	+1.9		
	1.400 (11)		185.2	181.3	+2.2		
	1.600 (11)		241.9	240.0	+0.8		
	1.715 (11)		277.9	284.4	-2.3		
19a. PA, N = .0251, M = 33.06, Q = 1408[e], G = 0.829							
	1.000 (11)	5.415	84.4	87.9	-4.0		
	1.200 (11)		121.4	121.9	-0.4		
	1.400 (11)		165.4	163.4	+1.2		
	1.600 (11)		216.0	214.7	+0.6		
	1.760 (11)		261.3	265.2	-1.5		

Table VI (continued)

19b. PA, Q = 1261[f]							
1.672 (16)	5.125	223.1	221.2	+0.8		
1.760 (16)		247.2	248.8	-0.6		
20a. Tetryl, N = .0270, M = 30.46, Q = 1351[g], G = 0.822						
1.000 (11)	5.478	85.3	87.1	-2.1		
1.200 (11)		122.9	121.4	+1.2		
1.400 (11)		167.3	164.6	+1.6		
1.600 (11)		218.5	218.8	-0.1		
1.700 (11)		246.7	251.5	-1.9		
20b. Tetryl, Q = 1420[h]						
1.644 (16)	5.615	236.3	235.9	+0.2		
1.730 (16)		261.8	264.3	-0.9		
21. Expl. D, N = .0285, M = 28.30, Q = 1082, G = 0.0807						
1.634 (16)	4.993	207.7	213.5	-2.8	207.0	+0.3
1.720 (16)		230.1	242.1	-5.2	229.3	+0.3
22a. DATB, N = .0278, M = 28.44, Q = 1246[i], G = 0.791						
1.000 (11)	5.233	81.5			81.7	-0.2
1.200 (11)		117.5			114.4	+2.7
1.400 (11)		159.7			155.0	+3.0
1.600 (11)		208.7			205.8	+1.4
1.788 (11)		260.6	282.0	-7.6	264.8	-1.6
22b. DATB, Q = 1151[j]						
1.000 (16)	5.030	78.4	76.5	+2.4		
1.200 (16)		113.0	109.9	+2.8		
1.400 (16)		153.6	151.8	+1.2		
1.600 (16)		200.3	205.0	-2.3		
1.745 (16)		238.8			238.6	+0.1
1.837 (16)		264.3	287.6	-8.1	267.8	-1.3
23. TATB, N = .0291, M = 27.20, Q = 1075, G = 0.791						
1.000 (11)	4.975	77.5			75.7	+2.4
1.200 (11)		111.7			107.4	+4.0
1.400 (11)		152.0			147.8	+2.8
1.600 (11)		198.5			199.0	-0.3
1.895 (11)		278.4	326.0	-14.6	297.3	-6.4
1.841 (16)		262.8			270.1	-2.7
1.938 (16)		291.2			304.3	-4.3
24. R-Salt, N = .0345, M = 23.00, Q = 1395, G = 0.790						
1.520 (16)	6.135	220.9			221.2	-0.1
1.600 (16)		244.8			246.6	-0.7
25. TNA, N = .0263, M = 30.00, Q = 1242, G = 0.789						
1.682 (16)	5.077	223.7			219.6	+1.9
1.770 (16)		247.7			245.6	+0.9
26. TNB, N = .0246, M = 32.00, Q = 1346, G = 0.787						
1.604 (16)	5.105	205.0	205.4	-0.2	198.9	+3.1
1.688 (16)		227.0	229.9	-1.3	221.1	+2.7

Table VI (continued)

27. DNPF, N = .0289, M = 26.93, Q = 1070, G = 0.778						
1.520 (16)	4.906	176.7			172.5	+2.4
1.600 (16)		195.8			193.3	+1.3
28. TNT, N = .0253, M = 28.52, Q = 1282, G = 0.722						
1.000 (k)	4.838	75.3	75.1	+0.3	76.2	-1.2
1.200 (k)		108.5	107.5	+0.9	106.7	+1.7
1.400 (k)		147.8	148.2	-0.3	145.4	+1.6
1.600 (k)		193.0	199.5	-3.3	194.3	-0.7
1.640 (11)		202.7	213.0	-4.8	205.7	-1.5
1.468 (16)		162.4			161.2	+0.7
1.651 (16)		205.6	214.4	-4.2	207.1	-0.7

Footnotes to Table VI:

a) See Appendix II for glossary of compound names and molecular formulas.

b) Values in parentheses for Compounds 1-6 are after -6% "correction" where $G_{arb} > 0.93$. See text.

c) Based on ΔH_f = +270.4 Kcal/mole. Probably incorrect.

d) Based on ΔH_f = +153.8 Kcal/mole. Probably incorrect.

e) Based on ΔH_f = -22.7 Kcal/mole. Misplaced decimal in input data.

f) Based on ΔH_f = -57.3 Kcal/mole.

g) Based on ΔH_f = -15.0 Kcal/mole.

h) Based on ΔH_f = +4.7 Kcal/mole.

i) Based on ΔH_f = -6.0 Kcal/mole.

j) Based on ΔH_f = -29.2 Kcal/mole.

k) TNT parameter results from ref. 11; RDX parameter results from ref. 16.

parameters) and P_{RUBY} (TNT parameters), e. g., 9.7% for TATB at 1.895 g/cc, 7.0% for RDX at 1.800 g/cc, however, it becomes necessary for each compound to decide which set of RUBY predictions is more appropriate to compare with the results of present calculations.

VIII. ANALYSIS OF RESULTS BASED ON "MORE APPROPRIATE" PARAMETERS

It has been mentioned that Mader designed the STRETCH BKW computor code[11,20] so as best to reproduce experimental measurements on RDX and TNT. Fundamental difficulties in finding a single set of α, β, κ and θ in Eq. (4) to accomodate the results on both explosives led him to employ two parameters sets (Table I), one of which reproduced the RDX measurements, the other the TNT measurements. To compute detonation properties of explosives other than RDX or TNT, Mader suggested the amount of solid carbon in the detonation products as a qualitative basis for deciding which parameter set to use. For explosives producing greater amounts of solid carbon in the detonation, the TNT parameters were believed to be the more appropriate; for compounds producing lesser amounts of solid carbon, the RDX parameters were considered the more suitable.

Since the quantity, G_{arb}, in the present discussions is an easily calculable measure of the amount of solid carbon produced in the detonation of an organic high explosive (i. e., weight proportion solid carbon = 1.000 - G), a somewhat more quantitative criterion of parameter suitability suggests itself. For RDX, $G_{arb} = 0.919$; for TNT, $G_{arb} = 0.722$; a median $G_{arb} = 0.820$. It seems reasonable, then, that for explosives with $G_{arb} > 0.820$ RUBY computations based on the RDX parameters might better accomodate experimental measurements, and that for explosives with $G_{arb} < 0.820$ the TNT parameters might lead to better correspondence.

Using G_{arb} greater or lesser than 0.820 as a basis for choosing between

sets of RUBY results, we may now compare the hand-calculations with computer predictions based on "more suitable" parameters, i. e., P_{calc} vs P_{RUBY} (RDX parameters) for compounds 1-10 and 12-20; P_{calc} vs P_{RUBY} (TNT parameters) for compounds 21-28:

Where $G_{arb} > 0.820$, 19 compounds, 72 data sets,
Average Difference = $\pm 3.07\%$,

Where $G_{arb} < 0.820$, 8 compounds, 31 data sets,
Average Difference = $\pm 1.77\%$,

All results, 27 compounds, 103 data sets,
Average difference = $\pm 2.68\%$

By way of comparison, differences between P_{calc} and P_{RUBY} (less suitable parameters) average $\pm 3.80\%$ for 11 compounds, 24 data sets.

One group of materials deserves special comment. It may be noted that the hand-calculated detonation pressures are in all cases significantly higher than the RUBY predictions for the overoxidized (Cmpds. 1-3), CO_2-balanced (Cmpd. 4) and near-CO_2-balanced explosives (Cmpds. 5,6). For these six compounds (19 data sets), the average difference between P_{calc} (Eq. 8) and P_{RUBY} is +6.54% (always positive). In Appendix III we shall offer arguments that these "errors" do not necessarily reflect any basic inadequacy of Eq. (8), but rather that the RDX parameters in RUBY computations may be inherently unsuitable for near-CO_2-balanced explosives.

For purposes of achieving closer correspondence with RUBY, however (and with the reservation that this "correction" is not necessarily applicable for the prediction of actual detonation parameters), the following additional step may be incorporated into the present method of calculation:

Where $G_{arb} > 0.93$, subtract 6% from P_{calc} (Eq. 8). (16)

Calculated detonation pressures and % differences incorporating this "correction" are given in parentheses in Table VI for Compounds 1-6. If these hand-calculated

values are used, the results break down as follows:

Where G_{arb} = 0.961 to 1.000, RDX parameters and a -6% correction, Average Difference = ±1.64%

Where G_{arb} = 0.822 to 0.919, RDX parameters, Average Difference = ±1.82%

Where G_{arb} = 0.722 to 0.807, TNT parameters, Average Difference = ±1.77%

All results, Average Difference = ±1.77%

An alternative method of comparing the results of Eq. (8) with RUBY is shown in Fig. 1, wherein values of P_{RUBY}/φ_{arb} are plotted against ρ_o^2. The solid line is of slope 15.58 and passes through the origin, and thus represents Eq. (8). Corresponding to "correction" (16), values of P_{RUBY} are divided by a factor of 0.94 where $G_{arb} > 0.93$. It is seen that only the single data point representing TATB at 1.895 g/cc differs by more than 5% from the calculated value.

Figure 1 near here

In the light of our earlier observation that N_{arb}, M_{arb} and Q_{arb} correspond closely to RUBY values at higher but not lower loading densities and our tentatively having set ρ_o = 1.4 g/cc as a lower limit of applicability of the method, it is also of interest to consider how differences between P_{calc} and P_{RUBY} are affected by ρ_o. The breakdown of results, after the -6% "correction" at $G_{arb} > 0.93$, is as follows:

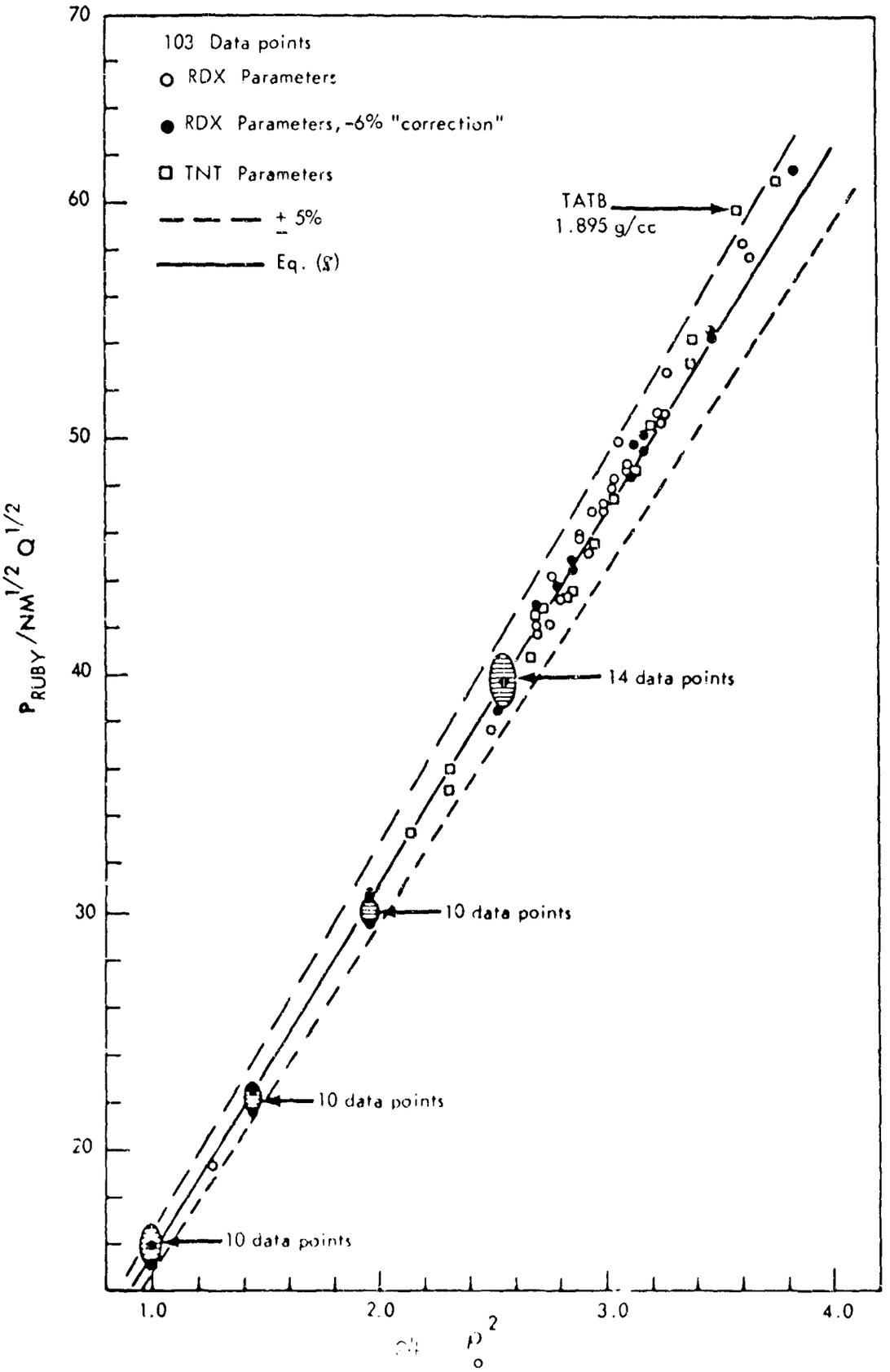
Where $\rho_o > 1.399$, Average Difference = ±1.66%,

Where ρ_o = 1.000 to 1.200, Average Difference = ±2.11%.

Although "errors" are indeed slightly greater at the lower densities, the trend is not strong and correspondence between Eq. (8) and RUBY is still surprisingly good down to 1.00 g/cc. That values of N, M and Q from the $[H_2O–CO_2]$ arbitrary should differ from RUBY's N, M and Q at the lower densities by such large amounts as are shown in Table V, yet lead to such good agreement in P as is shown in Table VI, raises some interesting questions. These will be discussed

NOLTP 67-66

FIG. 1 Comparison of Eq. (8) with RUBY-computed detonation pressures



in detail in the next paper of this series. Subsequent papers will also include a comparison of calculations by the present method with experimental detonation pressures and further evidence to support our simplified scheme for calculation of detonation velocities (Eq. 9).

IX. SUMMARY OF THE METHOD

Given the elemental composition, loading density and an estimate of the heat of formation of a C-H-N-O explosive, it is possible to estimate the detonation pressure by the following simple sequence of operations:

a) Calculate N_{arb}, M_{arb} and Q_{arb} from Eqs. (13), (14), and (15); multiply N_{arb} by M_{arb} to get G_{arb}.

b) Substitute N_{arb}, M_{arb} and Q_{arb} into Eq. (8); solve for P_{calc}.

c) Where correspondence with RUBY (but not necessarily with actual detonation pressures) is desired, subtract 6% from P_{calc} if G_{arb} is greater than 0.93.

At the current "state-of-the-art", such estimates warrant at least the same, and in some cases possibly greater reliance than the results of complex machine computations (see Appendix III and subsequent papers).

APPENDIX I. The Dependence of Pressure on Temperature in the Kistiakowsky-Wilson Equation of State with Mader's RUX Parameters.

In the special case of CO_2-balanced or overbalanced explosives, no solid carbon is produced and G = 1.00. Eq. (7), with Mader's RUX parameters, becomes:

$$P/N = 0.08205\ T\ \rho\ \left[1 + \frac{150.1\ \rho}{(T + 400)^{0.5}}\ e^{24.0\rho/(T + 400)^{0.5}}\right], \qquad (A\text{-}1)$$

where ρ is the compressed gas density. This dependence of P/N on ρ and T is shown in Table A-I in the range of temperatures and densities of interest in detonation calculations.

Table A-I. Values of P/N at Various Temperatures and Densities

ρ	$(P/N)_{4500^\circ}$	$(P/N)_{2100^\circ}$	$(P/N)_{1200^\circ}$
1.60	4,099	3,130	2,628
2.00	7,025	5,748	5,104
2.40	11,270	9,842	9,219
2.80	17,245	16,032	15,818
3.20	25,468	25,160	26,121

In this case, N is relatively independent of T since there is no solid carbon to participate in equilibria (10) and (11). For C-J detonations, P is therefore a function of ρ and T for the given explosive, the appropriate values being formally determined by application of the hydrodynamic equation and the C-J condition. However, the RUBY print-outs show that the compressed density, ρ_J, is mainly a function of ρ_o and only weakly dependent on Q or the elemental composition so that, for a wide variety of C-H-N-O explosives, RUBY's ρ_o's and ρ_J's satisfy the relationship,

$$\rho_J/\rho_o = 1.470 - .05625\ \rho_J\ , \qquad \text{(A-2)}$$

to within several tenths of one percent over the entire range of loading densities studied.

If Eq. (A-2) is substituted into (A-1) the result gives the approximate P, T states which can be satisfied by a given loading density. To show how insensitive the detonation pressure is to the value of the detonation temperature which is determined, extreme values of T have been used to generate Table A-II.

Table A-II. Dependence of P on T in Eq. (A-1) at Various Loading Densities.

ρ_o	$P_{4500°}/P_{2100°}$	$P_{4500°}/P_{1200°}$
1.16	1.310	1.560
1.47	1.222	1.376
1.80	1.145	1.222
2.13	1.076	1.090
2.48	1.012	0.975

Since most detonation temperatures calculated by RUBY fall within the range 2000 to 4000°K, it is apparent from Table A-I that an estimate of the detonation temperature to within 10% at the lower densities would fix P_J to within about ±2-3% and at higher densities the error would become progressively smaller.

The more general case where $G \neq 1.00$ requires a more complex analysis of interrelationships between RUBY's ρ_o, ρ_J, ρ_g, N_s and V_s and between P, N, G and T, but the conclusions are essentially the same. Dependence of P on T is not strong at the lower densities and becomes progressively weaker as ρ_o increases, until at ρ_o = ca 2.4 g/cc the inversion in sign of $\Delta P/\Delta T$ is observed. Such very weak dependence of P on T above 1.80 g/cc as is shown in Table A-II may signal a lessening adequacy of Mader's RDX parameters at the higher densities and account for the upward trend in P_{RUBY} relative to P_{calc} (Eq. 8) at 1.85–1.96 g/cc in Figure 1.

Such results may also suggest that, although excellent as an interpolative tool as was intended by RUBY's designers (i. e., for explosives with compositions and properties between RDX and TNT, see also Appendix III), the RUBY code may be less satisfactory in extrapolative situations. Various RUBY users have computed

detonation properties of hypothetical explosives at predicted densities as high as 2.1-2.2 g/cc, and have used the results as a basis for extended synthesis programs. It is now suggested that predictions of explosive properties based on such computations are subject to serious question.

Similar analyses of interrelationships between other of the quantities in RUBY print-outs which interact to produce P_{RUBY} have been carried out. These have allowed a series of approximations whereby Eqs. (7) and (A-1) are modified to yield still another expression, which has its roots in the behavior of the K-W equation of state, but which closely reproduces the P-N-M-Q-ρ_o relationships in empirical Eq. (8). The reasoning behind these approximations is rather involved and of probable interest to only a limited group of readers; their detailed discussion will therefore be deferred to a subsequent paper in this series.

APPENDIX II. Glossary of Compound Names and Molecular Formulas.

1. TNM, CN_4O_8, tetranitromethane
2. BTNEN, $C_4H_4N_8O_{14}$, bis(2,2,2-trinitroethyl)nitramine
3. NG, $C_3H_5N_3O_9$, nitroglycerine, glycerol trinitrate
4. BTNEU, $C_5H_6N_8O_{13}$, bis(2,2,2-trinitroethyl)urea
5. TNETB, $C_6H_6N_6O_{14}$, 2,2,2-trinitroethyl 4,4,4-trinitrobutyrate
6. PETN, $C_5H_8N_4O_{12}$, pentaerithritol tetranitrate
7. RDX, $C_3H_6N_6O_6$, cyclotrimethylene trinitramine, 1,3,5-triaza-1,3,5-trinitrocyclohexane
8. HMX, $C_4H_8N_8O_8$, cyclotetramethylene tetranitramine, 1,3,5,7-tetraza-1,3,5,7-tetranitrocyclooctane
9. DINA, $C_4H_8N_4O_8$, di(2-nitroxyethyl)nitramine
10. TNTAzB, $C_6N_{12}O_6$, 1,3,5-triazido-2,4,6-trinitrobenzene
11. NQ, $CH_4N_4O_2$, nitroguanidine

12. EDNA, $C_2H_6N_4O_4$, ethylene dinitramine, 1,2-di(nitramino)ethane

13. RDX/TNT, 77/23, $C_{5.04}H_{7.46}N_{6.88}O_{7.75}$, Cylcotol

14. HMX/TNT, 76/24, $C_{6.84}H_{10.03}N_{9.22}O_{10.43}$, Octol

15. DNPN, $C_6H_{10}N_6O_{10}$, bis(2,2-dinitropropyl)nitramine

16. HNsB, $C_6H_6O_6$, hexanitrosobenzene, benzotrifuroxan

17. NM, CH_3NO_2, nitromethane

18. RDX/TNT, 64/36, $C_{6.85}H_{8.75}N_{7.65}O_{9.30}$, Composition B

19. PA, $C_6H_3N_3O_7$, picric acid, 2,4,6-trinitrophenol

20. Tetryl, $C_7H_5N_5O_8$, N-methyl-N-nitro-2,4,6-trinitroaniline

21. Expl. D, $C_6H_6N_4O_7$, ammonium picrate

22. DATB, $C_6H_5N_5O_6$, 1,3-diamino-2,4,6-trinitrobenzene

23. TATB, $C_6H_6N_6O_6$, 1,3,5-triamino-2,4,6-trinitrobenzene

24. R-Salt, $C_3H_6N_6O_3$, cyclotrimethylene trinitrosamine, 1,3,5-triaza-1,3,5-trinitrosocyclohexane

25. TNA, $C_6H_4N_4O_6$, 2,4,6-trinitroaniline, picramide

26. TNB, $C_6H_3N_3O_6$, 1,3,5-trinitrobenzene

27. DNPF, $C_{10}H_{12}N_4O_{12}$, bis(2,2-dinitropropyl) fumarate

28. TNT, $C_7H_5N_3O_6$, 2,4,6-trinitrotoluene

APPENDIX III. The -6% "Correction" at $G_{arb} > 0.93$.

The reasoning behind our suggestion that the need for the -6% correction for near-CO_2-balanced explosives is not necessarily in consequence of any basic inadequacy of Eq. (8) is as follows: At most loading densities currently under

consideration, RDX parameters lead to higher values of P_{RUBY} than TNT parameters (see Table VI), the difference increasing at the higher loading densities[21]. It has been mentioned that, extending Mader's reasoning, RDX parameters are "exactly suitable" at $G_{arb} = 0.919$ and TNT parameters are "exactly suitable" at $G_{arb} = 0.722$. At other values of G_{arb} neither parameter set is "exactly suitable" but, setting G_{arb} greater or lesser than 0.820 as a criterion for choice, one or the other parameter set is "more appropriate".

"Exact suitability" at all values of G_{arb} would require either an infinite number of K-W parameter sets, or equations which adequately expressed the parameters as continuous functions of G or some other appropriate property of the explosive. Although we are not now in a position to offer such equations, it is nevertheless profitable to consider a quantity, P^{*}_{RUBY}, which would represent the pressure predicted by the computor if given as input information "exactly suitable" values of α, β, κ and θ.

From the relationship between RDX-parameter RUBY results and TNT-parameter results, it follows that at increasing values of G_{arb} between 0.722 and 0.919, P_{RUBY} (RDX parameters) should show a decreasingly positive bias, and P_{RUBY} (TNT parameters) should show an increasingly negative bias relative to P^{*}_{RUBY}. On detailed examination of Table VI, such trends between P_{RUBY} and P_{calc} (Eq. 8) may readily be discerned and it is now suggested that average differences would be even smaller if comparisons were between P_{calc} and such a P^{*}_{RUBY}.

Extending the same reasoning, P_{RUBY} (RDX parameters) should run increasingly low relative to P^{*}_{RUBY} at increasing values of G_{arb} above 0.919. In other words, given "exactly suitable" parameters, the computor would predict higher pressures for overoxidized, CO_2-balanced and near-CO_2-balanced explosives than are reported in refs. 11 and 16. Although we cannot now say whether such increases would be

sufficient to offset the "errors" in Table VI for compounds 1-6, we strongly suspect that such might be the case.

ACKNOWLEDGEMENTS

The authors are indebted to Messers. N. Coleburn, J. W. Enig, F. Petrone and Dr. H. Sternberg as well as to the groups at LRL and LASL for helpful discussions. Special thanks must also be expressed to Mr. H. Hurwitz for his patience in explaining the intricacies of detonation computations to an organic chemist (M. J. K.) and to Drs. Donna Price and J. E. Ablard for pointing out many appropriate references, editing preliminary drafts and helping to put the work in perspective. The work was carried out under NOL Foundational Research Task FR-44.

Footnotes and References:

1) H. B. Levine and R. E. Sharples, Operator's Manual for RUBY, Lawrence Radiation Laboratory Report, UCRL-6815 (1962).

2) For detailed references and a brief general discussion of other equations of state used in condensed phase detonation problems, see S. J. Jacobs, ARS Journal, 30, 151 (1960).

3) J. O. Hirschfelder and W. E. Roseveare, J. Phys. Chem., 43, 15 (1939).

4) J. O. Hirschfelder, F. G. McClure and C. F. Curtis, OSRD Report 547 (1942).

5) J. Taylor, Detonation in Condensed Explosives (Oxford University Press, London, 1052).

6) H. Jones and A. R. Miller, Proc. Roy. Soc., A-194, 480 (1948).

7) G. B. Kistiakowsky and E. B. Wilson, Jr., The Hydrodynamic Theory of Detonation and Shock Waves, OSRD Report 114 (1941).

8) R. D. Cowan and W. Fickett, J. Chem. Phys., 24, 932 (1956).

9) S. R. Brinkley and E. B. Wilson, Jr., Revised Method of Predicting the Detonation Velocities in Solid Explosives, OSRD Report 905 (1956).

10) E. A. Christian and H. G. Snay, Analysis of Experimental Data on Detonation Velocities, U. S. Naval Ordnance Laboratory Report, NavOrd-1508 (1951).

11) C. L. Mader, Detonation Properties of Condensed Explosives Computed Using the Becker-Kistiakowsky-Wilson Equation of State, Los Alamos Scientific Laboratory Report, LA-2900 (1963).

12) These, now, are the "geometrical" covolume factors of ref. 8. The arguments for increasing the k_i's of H_2O and NH_3 are included in a classified report by these authors.

13) W. Fickett, Detonation Properties of Condensed Explosives Calculated with an Equation of State Based on Intermolecular Potentials, Los Alamos Scientific Laboratory Report, LA-2712 (1962).

14) M. H. Rice and J. M. Walsh, J. Chem. Phys., 26, 825 (1957).

15) V. N. Zuberov and G. S. Telegin, Doklady Akad. Nauk SSSR, 142, 309 (1962); Soviet Phys. Doklady, English Transl. 7, 34 (1962).

16) RUBY results referred to in the present paper are by H. Hurwitz of this laboratory and have not yet been reported elsewhere. We are grateful to Mr. Hurwitz for making this information available.

17) For reasons which are as yet unresolved, however, RUBY and STRETCH BKW, given the same input information for the same explosive at the same loading density, will report slightly different Chapman-Jouguet densities. Though small, the differences are significant in their effects on C-J pressures, the problem being more pronounced (differences of several percent in P) with underbalanced explosives at higher loading densities. Compare, for example, the results from refs. 11 and 16 for HMX and TATB in Table VI.

18. Private communication, Dr. L. Seely, Stanford Research Institute.

Footnotes and References (continued):

19) The position of this equilibrium being a sensitive function of density, however, it would tend to introduce complications at $\rho_o < 1.0$ g/cc.

20) C. L. Mader, Detonation Performance Calculations Using the Kistiakowsky-Wilson Equation of State, Los Alamos Scientific Laboratory Report, LA-2613 (1961).

21) Differences between RUBY computations based on the two parameter sets depend strongly on loading density. At about 1.15 g/cc, both parameter sets give about the same results. As loading densities increase above this value, the RDX parameters give increasingly higher values of P than the TNT parameters, and at lower densities the converse is the case but to a lesser extent.

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)
U.S. Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland

2a REPORT SECURITY CLASSIFICATION
Unclassified

2b GROUP

3 REPORT TITLE
The Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of C-H-N-O Explosives.

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

5 AUTHOR(S) (Last name, first name, initial)
Mortimer J. Kamlet and S. J. Jacobs

6 REPORT DATE
July 19

7a TOTAL NO OF PAGES
49

7b NO OF REFS
21

8a CONTRACT OR GRANT NO

b PROJECT NO MAT 03L 000 R011
01 01
FR 44

c

d

9a ORIGINATOR'S REPORT NUMBER(S)
67-66

9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10 AVAILABILITY LIMITATION NOTICES
[illegible] is unlimited.

11 SUPPLEMENTARY NOTES

12 SPONSORING MILITARY ACTIVITY
U.S. Naval Ordnance Systems Command

13 ABSTRACT Detonation pressures of C-H-N-O explosives at initial densities above 1.0 g/cc may be calculated by means of the simple empirical equation, $P=K\rho_0^2\varphi$, $K=15.58$, $\varphi=NM^{\frac{1}{2}}Q^{\frac{1}{2}}$; detonation velocities by the equation, $D=A\varphi^{\frac{1}{2}}(1+B\rho_0)$, $A=1.01$, $B=1.30$. N is the number of moles of gaseous detonation products per gram of explosive; M is the average molecular weight of these gases; Q is the chemical energy of the detonation reaction (ΔH_c per gram); and ρ_0 is the initial density. Values of N, M and Q may be estimated from the [H_2O-CO_2] arbitrary decomposition assumption, so that the calculations require no other input information than the explosive's elemental composition, heat of formation and loading density. Detonation pressures derived in this manner correspond quite closely to values predicted by a computer code known as RUBY, which employs the most recent parameters and covolume factors with the Kistiakowsky-Wilson equation of state.

DD FORM 1 JAN 64 1473

UNCLASSIFIED
Security Classification

Unclassified
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Detonation pressure						
Detonation velocity						
RUBY computer code						
Explosives						
Detonations						
Simplified calculations						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee Department of Defense activity or other organization *(corporate author)* issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

_____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

_____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

_____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES. Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.

UNCLASSIFIED
Security Classification